

III.A.12 SOFC Cathode Materials Development at PNNL

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Objectives

- Develop solid oxide fuel cell (SOFC) cathode materials and microstructures offering low polarization losses and long-term stability at intermediate SOFC operating temperatures (650-800°C).
- Improve understanding of mechanisms affecting cathode performance, including both intrinsic factors (e.g., composition, microstructure) and extrinsic factors (e.g., Cr poisoning).

Approach

- Synthesize, process, and characterize candidate SOFC cathode compositions.
- Quantify performance of SOFC cathode materials on anode-supported cells.
- Evaluate effects of various interconnect alloys and Cr sources on cathode performance.

Accomplishments

- Evaluated effects of various current collectors on Sr-doped lanthanum ferrite (LSF) cathode performance.
- Obtained 2000 hours stable performance for Sr-doped lanthanum manganite (LSM)/samarium-doped ceria (SDC) composite cathode.

Future Directions

- Complete joint study (with Argonne National Lab and General Electric) on Cr poisoning of LSM cathodes.
- Investigate effects of various current collectors on cathode performance.
- Investigate degradation mechanisms of lanthanum cobalt-ferrite based cathodes.
- Optimize performance and stability of LSM-based cathodes.

Introduction

Minimization of cathodic polarization losses represents one of the greatest challenges to be overcome in obtaining high, stable power densities from SOFCs. Cathodic polarization exhibits a high activation energy relative to other internal power losses, so the need to improve cathode performance becomes increasingly important as the targeted SOFC operating temperature is reduced. The severe environmental conditions experienced by the cathode during operation limit the number of likely candidate materials. In particular, the cathode material must be

stable at the SOFC operating temperature in air, and it must have high electronic conductivity, high catalytic activity for the oxygen reduction reaction, and a thermal expansion compatible with the SOFC electrolyte. Chemical interactions with the electrolyte and interconnect materials must be minimal. In addition, the cathode material must have a stable, porous microstructure so that gaseous oxygen can readily diffuse through the cathode to the cathode/electrolyte interface.

For high-temperature SOFCs operating at around 1000°C, the preferred cathode material is A- and B-

site doped lanthanum manganite, which offers adequate electrical conductivity and electrocatalytic activity, reasonable thermal expansion, and stability in the SOFC cathode operating environment. For SOFCs operating at substantially lower temperatures, such as 650–800°C, alternative cathode materials may be required. Alternative perovskite compositions – typically containing La on the A site and transition metals such as Co, Fe, and/or Ni on the B site – have received attention. In general, they offer higher oxygen ion diffusion rates and exhibit faster oxygen reduction kinetics at the electrode/electrolyte interface than lanthanum manganite, but are subject to degradation of performance over time.

Approach

Cathode powders were synthesized using the glycine-nitrate combustion technique. The powders were processed to obtain the desired particle size distribution, and then sintered onto anode-supported yttria-stabilized zirconia (YSZ) membranes with an SDC interlayer. After attachment of current collectors, the resulting cells were placed into test fixtures, and their current-voltage data was evaluated. After cell tests were completed, the cells were analyzed by scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS).

Results

One area of focus was the investigation of the effects of various current collector/contact materials on performance of LSF cathodes. Figure 1 compares power density data at 0.7 V/750°C (over a 500-hour period) for several different cathode current collectors (Pt, Ag, Au and Crofer22 APU coated with a spinel protection layer) utilized in conjunction with nominally identical anode-supported cells with LSF cathodes.

LSF Cathode with Pt Current Collector

For the LSF-20 based cell utilizing a Pt cathode current collector, rapid degradation was observed [~22% increase in area-specific resistance (ASR)] over the initial 20–30 hours of operation, followed by equally rapid cell conditioning and eventual performance stability after ~200 hours. These performance characteristics are actually typical for LSF cells utilizing Pt current collectors, though

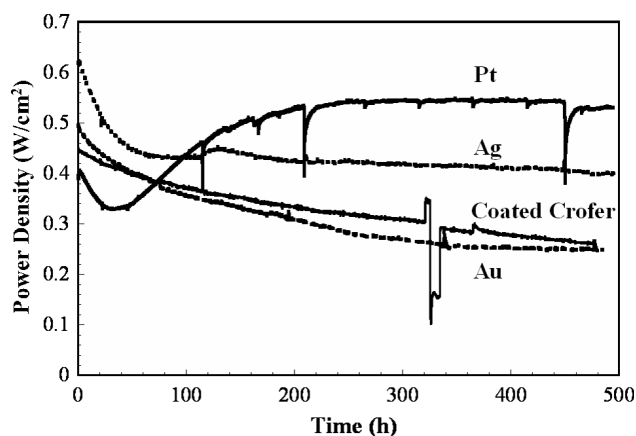


Figure 1. Long-Term Performance for LSF-Based Cells Utilizing Platinum, Silver, Gold and Spinel-Coated Crofer22 APU Cathode Current Collectors

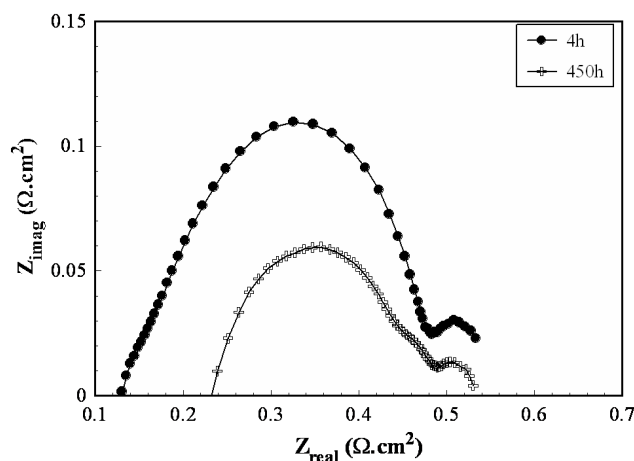


Figure 2. Impedance Data for Anode-Supported SOFC with LSF-20 Cathode and Pt Cathode Current Collector

mechanisms responsible for the initial degradation have not been established. Impedance data for this cell are shown in Figure 2. The ohmic resistance of the cell (high frequency intercept) increased in magnitude over time. SEM analysis of the tested cell revealed Pt deposition at the LSF-SDC interface; this is likely the result of $\text{PtO}_2(\text{g})$ evaporation from the Pt surface and subsequent reduction at the LSF-SDC interface. The improvement in cathode performance over time may have been due to a catalytic effect of the deposited Pt on the oxygen reduction kinetics. The increasing ohmic resistance during the duration of the cell test may also be related to Pt volatility. Volatilization of Pt may have resulted in reduced

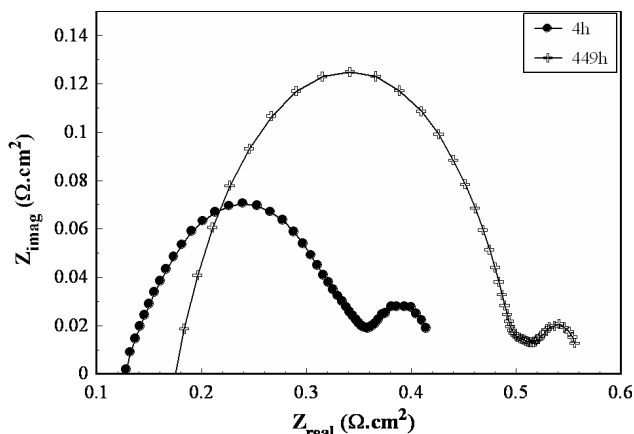


Figure 3. Impedance Data for Anode-Supported SOFC with LSF-20 Cathode and Ag Cathode Current Collector

contact area between the LSF cathode and the Pt current collector, and hence increased contact resistance.

LSF Cathode with Ag Current Collector

For the cell with a Ag current collector, the initial ASR was substantially lower than that of the LSF-Pt cell; however, similar to the LSF-Pt sample, the LSF-Ag cell subsequently exhibited rapid initial degradation. Impedance data for this cell are shown in Figure 3. As for the LSF-Pt cell, the ohmic resistance increased over time. Significant Ag migration to the LSF-SDC interface was observed in the tested cell, and it would seem likely that movement of Ag from the Ag current collector to the LSF-SDC increased the contact resistance at the current collector/cathode interface.

The deposition characteristics of the LSF-Ag cell appeared to be somewhat different compared to the LSF-Pt sample in that the Ag appeared to migrate deeply into the pores in the SDC layer, while Pt deposited primarily at the active LSF-SDC interface. In fact, there were regions of the SDC interlayer that were completely infiltrated with the Ag metal.

LSF Cathode with Au Current Collector

The cell with an LSF cathode and Au current collector exhibited continuous degradation which was most rapid over the first 100 hours. Impedance data for this cell are shown in Figure 4. Unlike the LSF-Pt and LSF-Ag cells, the LSF-Au cell showed

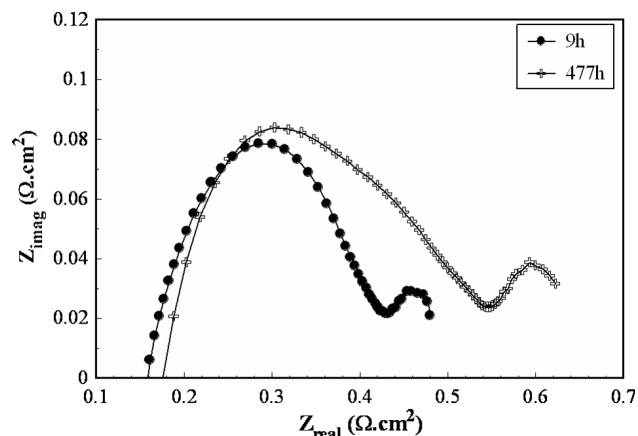


Figure 4. Impedance Data for Anode-Supported SOFC with LSF-20 Cathode and Au Cathode Current Collector

little change in ohmic resistance during the 500-hour test period. This may be related to the lack of Au volatilization from the Au-cathode interface; SEM analysis of the tested cell found no evidence of migration of Au to the cathode-electrolyte interface. The degradation of the LSF-Au cell is somewhat difficult to explain. Rigorous SEM/EDS analysis was conducted on the pre- and post-tested cells utilizing each of the noble metal current collectors, but no prominent differences were observed in either microstructure or composition to account for the continuous degradation of the LSF-Au or LSF-Crofer22 APU cells. It is possible that LSF (or the combination of an LSF cathode with an SDC interlayer on an anode-supported YSZ membrane) is subject to some form of intrinsic degradation that is suppressed when sufficient noble metal is deposited at the cathode-electrolyte interface. The fact that cell tests with a spinel-coated Crofer22 APU current collector and LSF contact paste showed similar degradation to cell tests with a Au current collector is consistent with the explanation that, in the absence of Pt or Ag, LSF is subject to an intrinsic degradation of performance.

Conclusions

Based on the results of this study, Au appears to be the most stable current collector choice for the measurement of intrinsic properties of LSF cathodes, as both Ag and Pt appear to affect the cathode performance by accumulating at the LSF-SDC interface.

FY 2005 Presentations

1. "SECA Core Technology Program – PNNL: Cell Materials Development," J.W. Stevenson, S.P. Simner, M. Anderson, O.A. Marina, and A. Mueller, 6th Annual SECA Alliance Workshop, Pacific Grove, CA, April 17-22, 2005.
2. "Cathode-Metallic Interconnect Compatibility," S.P. Simner, M. Anderson, G. Xia, Z. Yang, and J.W. Stevenson, 2nd International Symposium on Solid Oxide Fuel Cell (SOFC) Materials and Technology, 29th International Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, January 23-28, 2005.
3. "Cathode Development at PNNL," S.P. Simner, M. Anderson, Z. Yang, G. Xia, and J.W. Stevenson, SECA Core Technology Program Review Meeting, Tampa, FL, January 27-28, 2005.
4. "SOFC Cathode Interaction with Volatile Chromia Sources," S. Simner, M. Anderson, J.-Y. Kim, K. Meinhardt, Vince Sprenkle, and J.W. Stevenson, 2004 Fuel Cell Seminar, San Antonio, TX, November 1-5, 2004.

FY 2005 Publications

1. S.P. Simner, M.D. Anderson, G.-G. Xia, Z. Yang, L.R. Pederson, and J.W. Stevenson, "SOFC Performance with Fe-Cr-Mn Alloy Interconnect," J. Electrochem.Soc., 152, A740 (2005).
2. S.P. Simner, M.D. Anderson, and J.W. Stevenson, "La(Sr)FeO₃ SOFC Cathodes with Marginal Copper Doping," J. Am. Ceram. Soc., 87, 1471 (2004).